

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 May 2002 (23.05.2002)

PCT

(10) International Publication Number
WO 02/40988 A1

(51) International Patent Classification: G01N 30/30

[IT/IT]: Via Don Milani, 21/B, I-20063 Cernusco sul Naviglio (IT). **FACCETTI, Riccardo** [IT/IT]; Via Paolo VI, 29, I-23900 Lecco (IT). **MAGNI, Paolo** [IT/IT]; Via S. Antonio, 2, I-20045 Besana Brianza (IT).

(21) International Application Number: PCT/IB01/02037

(22) International Filing Date: 29 October 2001 (29.10.2001)

(25) Filing Language: English

(74) Agent: **VALENTINI, Giuliano**; Marietti, Gislon e Trupiano S.r.l., Via Larga, 16, I-20122 Milano (IT).

(26) Publication Language: English

(81) Designated State (national): US.

(30) Priority Data:

MI2000A002449

15 November 2000 (15.11.2000) IT

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(71) Applicant (for all designated States except US):
THERMO FINNIGAN ITALIA S.P.A. [IT/IT]; Strada Rivoltana, I-20090 Rodano (IT).

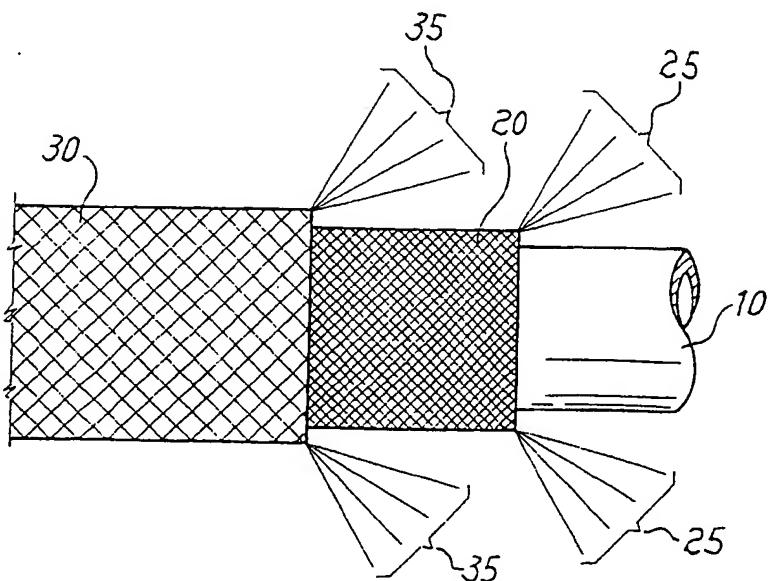
Published:
— with international search report

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ZILIOLO, Giacinto**

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CHROMATOGRAPHY COLUMN



WO 02/40988 A1

(57) Abstract: Described herein is a direct-heating column assembly for chromatography, in which a capillary column is enveloped in a tubular mesh formed by a plurality of woven filaments.

"CHROMATOGRAPHY COLUMN"

Technical Field

The present invention relates to a chromatography column and, more in particular, a chromatography-column assembly of the direct-heating type.

Background Art

A number of technical solutions are already known in which the capillary column is subjected to direct heating by means of an electrically conductive element which is set in contact with the capillary column and electrically powered in a controlled way.

Such an approach makes it possible to obtain various advantages, among which the considerable reduction in the electrical energy required for heating the capillary column and the rapid response of the system to the temperature programs that are set in the course of the analysis.

A number of the various possibilities of obtaining direct heating of the column are, for example, illustrated in US patent No. US-A-5808178 and in the corresponding international patent application No. WO 97/14957 in the name of Thermedics. Among the various solutions proposed, an assembly is illustrated comprising a column made of fused silica inserted in a tube made of steel, the latter having an internal diameter greater than the external diameter of the column for enabling insertion of the column itself. The steel tube is in turn coated with an insulating sheath made of woven glass fibres.

Another example is described in the US patent No. US-A-5611846 by Overton *et al.* For heating the column, this document suggests inserting the column into a sheath together with a conductive filament, or else inserting the column directly into a tube made of conductive material. In a publication by the same authors ("Novel

Column Heater for Fast Capillary Gas Chromatography"; Overton *et al.*

- Journal of Chromatographic Science - Vol. 34 - December, 1996) it is emphasised that the proposed solution of inserting a capillary column directly into a tube made of conductive material is theoretically 5 preferable for obtaining optimal heating of the column itself, but it is also noted that this solution has proven impracticable due to breakages that occur in the proximity of the sealed ends of the column assembly. This is mainly due to the different thermal coefficients of expansion of the materials.

10 Other examples of column assemblies of a direct-heating type may be found in the US patent No. US-A-5114439 by Yost *et al.*, as well as in the US patent No. US-A-5005399 by Holtzclaw *et al.*. The columns illustrated in these documents are made of silica and coated with a layer of conductive material, in particular aluminium.

15 However, on account of the different coefficients of thermal expansion of the materials, there occur frequent breakages of the capillary column or of the conductive coating deposited thereon.

Another example of a direct-heating column for chromatography is illustrated in the US patent No. US-A-4484061 by Zelinka and Sims. 20 Wound in a spiral on the column is at least one thin film of conductive material enclosed between two electrically insulating films. Fixing to the column during fabrication is ensured by an adhesive, and the assembly is then further coated with a spiral sheath. A construction of this kind, in addition to being particularly complicated and laborious, 25 may prove far from suitable for withstanding high temperatures on account of the use of adhesives. In addition, in the absence of direct contact between the conductive heating material and the column, it is difficult to guarantee uniform heating of the column itself.

Given the above, the object of the present invention is to provide

a chromatography-column assembly that enables perfectly uniform direct heating of the column throughout its length.

Another object of the present invention is to provide a chromatography-column assembly capable of withstanding of direct 5 heating of the capillary column at high temperatures.

A further object of the present invention is to provide a particularly simple and economical method for making a direct-heating column assembly of the type referred to above.

Disclosure of Invention

10 These objects are achieved by the present invention, which relates to a direct-heating column assembly for chromatography, of the type comprising at least one capillary column and at least one element made of electrically conductive material in contact with the capillary column, characterised in that the element made of conductive 15 material comprises a plurality of filaments woven together to form a tubular mesh that envelops the capillary column. There is thus obtained a geometrical symmetry that is particularly effective for guaranteeing a uniform transmission of heat to the column and an optimal distribution of temperature over the entire surface thereof.

20 According to a peculiar aspect of the present invention, the inner surface of the tubular mesh made of electrically conductive material is set in close contact with the outer surface of the capillary column. The heating element made in the form of a tubular mesh, unlike the known solutions, enables a more intimate contact between the 25 column and the heating element also during sudden changes in temperature.

In addition, in the case where the mesh made of electrically conductive material is used not only as heating means but also as sensor means for detecting the temperature of the column, it is thus

possible to obtain also a high precision in the control of the temperature of the column.

The capillary column can be made of an electrically insulating material, such as fused silica, which is widely used for making capillary 5 columns designed for chromatography equipment. As an alternative, the capillary column can be also made of conductive material, in particular metal, and can be coated externally with electrically insulating material to prevent contact between the capillary column and the heating element.

10 The column assembly according to the invention further comprises a tubular coating sheath that envelops the tubular mesh made of electrically conductive material.

According to a possible embodiment, the tubular coating sheath, 15 consisting of electrically and thermally insulating material, is made up of a plurality of woven filaments. This enables the coating sheaths to be made with materials particularly resistant to heat, for example filaments made of ceramic fibre, glass fibre or other insulating material, thus affording the possibility of using the column also at relatively high temperatures.

20 The mesh structure of the heating element and of the coating sheath gives on the column assembly a high flexibility and enables compensation of the different thermal expansion of the materials without altering the performance of the column itself.

According to a possible embodiment, the insulating sheath can be 25 set in close contact with the outer surface of the tubular mesh made of electrically conductive material.

Alternatively, the tubular sheath made of insulating material can have a section of a diameter greater than the tubular mesh set on the column, in such a way as to enable the possible circulation of a heat-

exchange fluid for obtaining rapid cooling of the column, or else a more homogeneous distribution of heat throughout the column.

The invention further relates to a method for making a chromatography-column assembly of a direct-heating type,
5 characterised by providing the weaving of a plurality of filaments made of electrically conductive material to form a tubular mesh around a capillary column.

It is therefore possible to produce the column assembly according to the invention by weaving the tubular mesh made of electrically
10 conductive material directly on a capillary column made of fused silica or on a column made of metal coated externally with insulating material.

Also the formation of the tubular sheath of insulating coating on the tubular mesh made of electrically conductive material can be
15 produced equally simply in the same way.

The simplicity of construction of the column assembly according to the invention may thus be appreciated, as well as the possibility of obtaining the production of such a column assembly at limited costs.

Brief Description of Drawings

20 Further characteristics and advantages of the present invention will appear more clearly from the following description, provided purely by way of non-limiting illustrative example with reference to the attached drawings, in which:

- Figure 1 is a cross-sectional view of a column assembly according
25 to a possible embodiment of the invention;
- Figure 2 illustrates the composition of a portion of the column assembly of Figure 1;
- Figure 3 is a cross-sectional view of a column assembly according to an alternative embodiment of the invention; and

- Figure 4 illustrates the composition of a portion of the column assembly of Figure 3.

Modes for Carrying Out the Invention

With reference firstly to Figures 1 and 2, a column assembly 5 according to the present invention comprises a capillary column 10, made, for example, of fused silica, enveloped in a tubular mesh 20 made of electrically conductive material. The tubular mesh 20 is in turn surrounded by a tubular sheath 30 made of insulating material.

As an alternative to the embodiment here illustrated purely by way 10 of example, the capillary column 10 can also be made of metal, for instance steel or other suitable conductive metals, and be coated externally with insulating material, consisting, for example, of a polyamide sheath, to prevent contact between the metal capillary column and the tubular mesh 20.

15 The tubular mesh 20 is formed by weaving together a plurality of thin filaments 25 made of an electrically conductive material, such as nickel, or anyway any material, whether metallic or non-metallic, having suitable characteristics of electrical conductivity.

As compared to the known solutions, which provide a single 20 conductive wire set alongside the column or a conductive tube that houses the column inside it, the conductive element with tubular mesh offers a greater reproducibility of the electrical characteristics in that the variability of the parameters of these known conductive elements (section, length, contact, expansion, etc.) is greater than the 25 summation of the individual filaments that form the mesh.

Also to be considered is the advantageous possibility of making a heating element in form of tubular-mesh using woven filaments made of conductive materials having electrical and thermal characteristics different from one another. This enables production of a conductive

element having a "new electrical or thermal characteristic" that can be exploited in particular applications, for example a desired variation in overall resistivity of the heating element according to the temperature.

5 The conductive element made in the form of a mesh 20 is woven preferably in close contact with the column, without, however, being integral with it. The mesh can thus "be deformed" with respect to the column, following upon the difference of expansion of the individual conductive filaments with respect to the column, but the mesh

10 structure is intrinsically capable of absorbing such "deformations" without any breaks occurring at the ends of the assembly, as instead occurs in some solutions proposed in the known art for direct heating of the column, such as, for example, a tube made of electrically conductive material.

15 The greater flexibility of the assembly enables, in addition, other advantages, such as that of reducing the radius of curvature of the column assembly, as well as that of enabling the use of capillary columns having a relatively large internal diameter.

By supplying electrical energy to the ends of the tubular mesh 20 made of electrically conductive material, it is thus possible to obtain direct heating of the column 10 with perfectly homogeneous transmission of heat, thanks to the geometrical symmetry of the section. The tubular mesh 20 can also be used as sensor means for determining the temperature of the capillary column with high precision. For controlling the heating of the column it is advantageously possible to utilise a system such as the one described in the prior Italian patent application No. MI99A-002708 in the name of the same Applicant.

Wrapped around the tubular mesh 20 is a tubular coating sheath

30 formed by weaving a plurality of filaments 35 made of electrically insulating material, or more preferably a material simultaneously having electrical and thermal insulating characteristics. The filaments 35 can be made, for example, of ceramic fibre or glass fibre, which

5 are materials having the required insulating characteristics, in addition to having the capacity of withstanding high temperatures. For example, ceramic fibres can withstand temperatures higher than 500°C, in particular even up to a 1000°C. These temperatures are far higher than the maximum limit of the temperature range (from

10 approximately -100°C to approximately +450°C) to which a chromatography column of a known type is subjected during use.

Other materials having suitable insulating characteristics and characteristics of resistance to high temperatures may, however, be used.

15 In the embodiment illustrated in Figures 1 and 2, the tubular mesh 20 made of electrically conductive material is set in contact with the capillary column 10, and the tubular sheath 30 made of insulating material envelops the tubular mesh 20 that is in contact with it.

It should be emphasised that, in a column assembly thus made,

20 the heating element and the insulating sheath are not integral with one another even though they are set substantially in close mutual contact. This structure thus enables compensation of the inevitable differences in thermal expansion of the materials used, hence without any problems of breaking of the column assembly thus arising.

25 Figures 3 and 4 illustrate an alternative embodiment of the invention, for which the same reference numbers have been preserved for identifying parts in common with the previously illustrated embodiment.

As in the case of the previous embodiment, the column assembly

of Figures 3 and 4 comprises a capillary column 10 made of fused silica on which there is wound in close contact a tubular mesh 20 formed by filaments 25 made of conductive material. Also in this case, the capillary column 10 may, however, be made of metal and be 5 appropriately coated externally with electrically insulating material to prevent contact between the column 10 and the conductive element 20.

The assembly thus formed is housed inside of a tubular sheath 40 made of insulating material having an internal diameter greater than 10 the external diameter of the tubular mesh 20. This enables formation of a gap 45, in which a heat-exchange fluid can be made to circulate to speed up cooling of the column or to render distribution of the heat in the column assembly thus made more uniform.

The tubular insulating sheath 40 can, for instance, be made with a 15 film of plastic material, for example polyamide or other suitable plastic materials. Alternatively, the tubular sheath can be made in the form of a tube of plastic material, or else metallic material, with an internal coating made of plastic or, in any case, an electrically insulating material.

20 To make a column assembly according to the present invention it is possible to use machines of a known type that produce tubular meshes wound on supports of circular section, for instance the same machines used in the production of shielded electrical cables or the like, possibly modified to be suitable to treat the materials that 25 constitute the column assembly according to the invention.

The method of production of the column assembly according to the invention is particularly simple to put in practice. On the capillary column 10 there is first "woven", in close contact with the column, a tubular mesh 20 formed by a plurality of filaments 25 made of

conductive material.

On top of the tubular mesh 20, there can then be woven the tubular sheath 30, in close contact with the underlying mesh 20, by weaving together a plurality of filaments 35 made of insulating material to obtain a column assembly as illustrated in Figures 1 and 2.

Alternatively, the column assembly represented in Figures 3 and 4 can be obtained simply by sliding the column 10 with the respective tubular mesh 20 into the tubular insulating sheath 40.

There are thus produced, in a continuous way and at limited costs, column assemblies that can then be cut to obtain direct-heating columns for chromatographic equipment having any desired length.

Various modifications, above all as regards the materials, can be made with respect to the embodiments illustrated purely by way of example, without departing from the scope of the present invention.

For instance, filaments made of different insulating materials can be woven together to form the tubular coating sheath if it is desired to give particular properties on the coating itself. The tubular sheath 30 itself produced with the filaments 35 made of insulating material can possibly be formed with a diameter greater than that of the tubular mesh 20 and of the column 10 if it is desired to keep the insulating sheath 30 at a distance from the rest of the assembly, irrespective of whether there is provided the circulation of a heat-exchange fluid in the gap which is thus formed. If, however, the circulation of a fluid is provided in the gap, the seal of the "enlarged" sheath 30 may, for instance, be made with possible films of coating inside and/or outside the sheath 30.

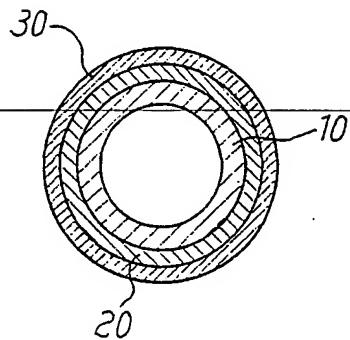
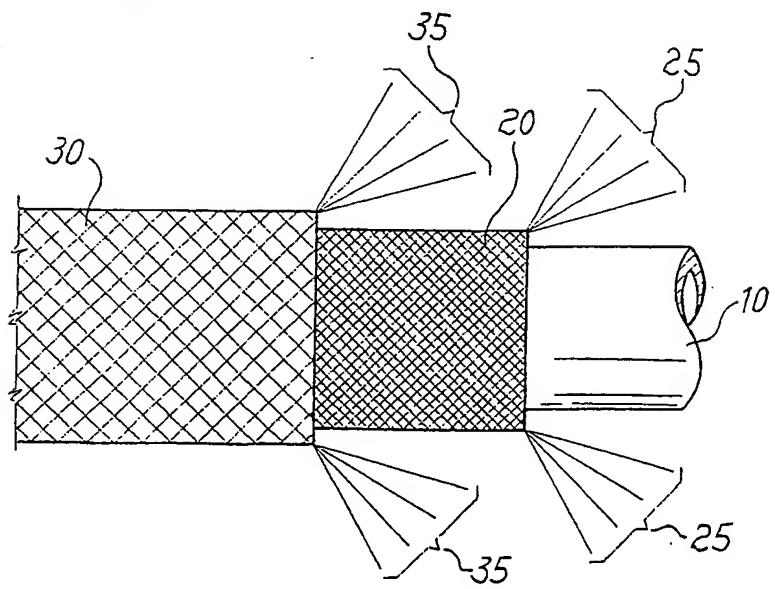
The embodiment of the column assembly according to the invention may be conveniently adapted to the configuration that a column has when it is installed in equipment for chromatography, i.e.,

the configuration of a winding with a number of turns.

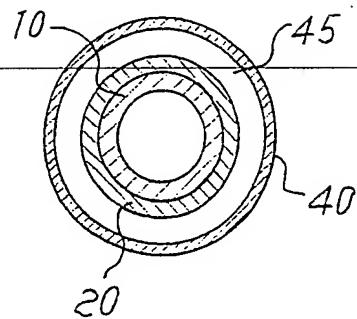
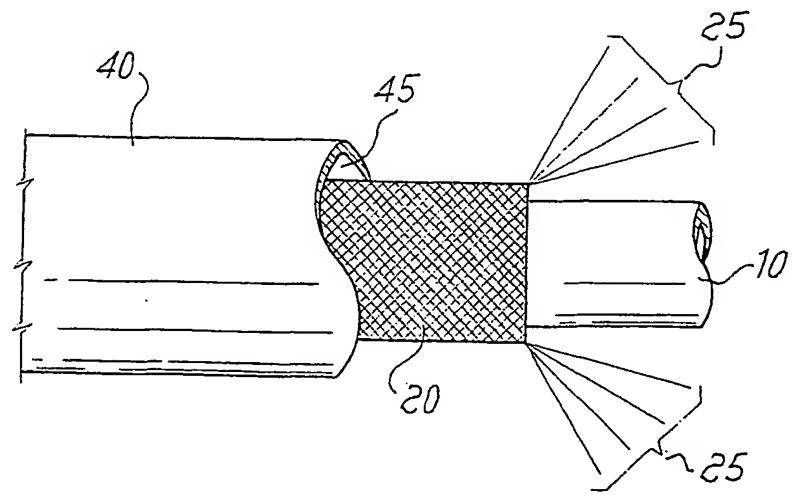
CLAIMS

1. A direct-heating column assembly for chromatography, of the type comprising at least one capillary column and at least one element made of electrically conductive material in contact with said capillary column, characterised in that said element made of conductive material comprises a plurality of filaments woven together to form a tubular mesh that envelops said column.
2. A chromatography-column assembly according to Claim 1, wherein the inner surface of said tubular mesh made of electrically conductive material is set in close contact with the outer surface of said capillary column.
3. A chromatography-column assembly according to Claim 1, wherein it further comprises a tubular coating sheath that envelops said tubular mesh made of electrically conductive material.
4. A chromatography-column assembly according to Claim 3, wherein said tubular coating sheath is made of electrically insulating material.
5. A chromatography-column assembly according to Claim 3, wherein said tubular coating sheath is made of thermally insulating material.
6. A chromatography-column assembly according to Claim 3, wherein said tubular coating sheath is made with a material capable of withstanding temperatures higher than 400°C.
7. A chromatography-column assembly according to Claim 3, wherein said tubular coating sheath made of insulating material is formed by a plurality of woven filaments.
8. A chromatography-column assembly according to Claim 3, wherein said tubular coating sheath made of insulating material is formed by a film.

1/2

Fig. 1Fig. 2

2/2

Fig. 3Fig. 4

INTERNATIONAL SEARCH REPORT

Application No.
NL/IB 01/02037A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N30/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data-base consulted during the international search (name of data-base and, where practical, search-terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 808 178 A (MACDONALD STEPHEN J ET AL) 15 September 1998 (1998-09-15) cited in the application column 3, line 50 -column 4, line 4; figures 4,5 ---	1,15
A	US 3 522 413 A (CHROW ALBERT E) 4 August 1970 (1970-08-04) abstract; figure 1 ---	1,15
A	US 5 744 206 A (RUSSEK JAIME ELLSTEIN ET AL) 28 April 1998 (1998-04-28) abstract; figures 1,2 column 2, line 46 ---	1,15
A	US 5 544 276 A (LOUX ALAN D ET AL) 6 August 1996 (1996-08-06) column 3, line 26-37 ---	1,15

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

31 January 2002

Date of mailing of the international search report

11/02/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Zinngrebe, U

Information on patent family members

TB 01/02037

Patent document cited in search report	Publication date		Patent family member(s)		Publication date
US 5808178	A 15-09-1998	EP WO	0876607 A1 9714957 A1		11-11-1998 24-04-1997
US 3522413	A 04-08-1970	US	3355572 A 3727029 A		28-11-1967 10-04-1973
US 5744206	A 28-04-1998	US	5712010 A		27-01-1998
US 5544276	A 06-08-1996	NONE			